

JPRS 70511

20 January 1978

U S S R

USSR AND EASTERN EUROPE SCIENTIFIC ABSTRACTS

CHEMISTRY

No. 58

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<b>BIBLIOGRAPHIC DATA SHEET</b>		1. Report No. JPRS 70511	2.	3. Recipient's Accession No.
4. Title and Subtitle  USSR AND EASTERN EUROPE SCIENTIFIC ABSTRACTS - CHEMISTRY No. 58				5. Report Date 20 January 1978
6.				8. Performing Organization Rept. No.
7. Author(s)				10. Project/Task/Work Unit No.
9. Performing Organization Name and Address  Joint Publications Research Service 1000 North Glebe Road Arlington, Virginia 22201				11. Contract/Grant No.
12. Sponsoring Organization Name and Address				13. Type of Report & Period Covered
				14.
15. Supplementary Notes				
16. Abstracts  The report contains abstracts and news items on adsorption phenomena, aerosols, alkaloids, analytica, electro- and biochemistry, coal gasification, combustion and explosives, environmental pollution, food technology, free radicals, ion exchange, organometallic and organophosphorus compounds, pesticides, industrial toxicology, petroleum processing technology, radiation chemistry, and related fields.				
17. Key Words and Document Analysis. 17a. Descriptors				
USSR Eastern Europe Chemical Analysis Organic Chemistry Physical Chemistry Inorganic Chemistry	Chemical Engineering Biochemistry Agricultural Chemistry Pharmacology Petrochemistry Radiation Chemistry Toxicology			
17b. Identifiers/Open-Ended Terms				
17c. COSATI Field/Group 7A, 7B, 7C, 7D, 7E, 6A, 6F, 60, 19A				
18. Availability Statement  Unlimited Availability Sold by NTIS Springfield, Virginia 22151		19. Security Class (This Report) <b>UNCLASSIFIED</b>	21. No. of Pages <b>44</b>	
		20. Security Class (This Page) <b>UNCLASSIFIED</b>	22. Price	

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No. 58

This serial publication contains abstracts of articles and news items from USSR and Eastern Europe scientific and technical journals on the specific subjects reflected in the table of contents.

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Analytical Chemistry

USSR

UDC 613.632+614.72)-074:546.48

EXTRACTION AND FLUOROMETRIC DETERMINATION OF CADMIUM IN OBJECTS IN THE ENVIRONMENT

Moscow GIGIYENA I SANITARIYA in Russian No 7, Jul 77 signed to press 29 Nov 76 pp 69-72

RADOVSKAYA, T. L., and KHAZEMOVA, L. A., candidates of chemical sciences, Sverdlovsk Institute of Labor Hygiene and Occupational Diseases

[Abstract] The luminescence method for cadmium assay compares favorably with other methods for its determination, photometric, polarographic and atomic absorption. A variation of this method, i.e., developed in the last 5 years consists of extraction and concentration of anions of halogen complexes of analyzed elements with triphenylmethane dyes. A modification of this method, used to determine Cd in water and atmospheric air at a light metallurgy installation, involves forming the Cd iodide complex in boiling ammonium phosphate solution, followed by extraction and concentration at pH 1.2-1.4 with pure benzene and thodamine. The organic phase is assayed by fluorimetry against a calibrated curve. The proposed method compares favorably with results obtained by polarographic and atomic absorption. A unique feature of the method is the elimination of interfering elements found with Cd in industrial wastes. It is also suggested for use in soils and biological specimens. References 3 (Russian).

USSR

UDC 613.298:678.4)-074

QUANTITATIVE SPECTROPHOTOMETRIC DETERMINATION OF KAPTAZ IN RUBBER PRODUCTS WHICH COME IN CONTACT WITH FOOD PRODUCTS

Moscow GIGIYENA I SANITARIYA in Russian No 7, Jul 77 signed to press 20 Jul 76 pp 68-69

SKVORODA, V. I., YAKIMENKO, N. F., and BELAYA, L. L., Minsk Oblast Sanepid Station

[Abstract] Kaptaz is a breakdown product of accelerators used in vulcanization of rubber used for food purposes. The maximum permissible level of kaptaz (0.15 mg/l) in products which contact foods has been established. Content of kaptaz must therefore be controlled. The authors have devised a spectrophotometric assay for kaptaz, in food-contacting items, which consists of constructing a calibrated graph of kaptaz content in chloroform solution, at various dilutions of a standard 10 mcm/ml solution. The test sample is extracted for kaptaz with chloroform and the extract assayed with a SF-16 spectrophotometer. The sensitivity of the method is 0.05 mg/l. Tests run on working samples give good results. Reference 1 (Russian).

USSR

UDC 632.955:543.544.42

DETERMINATION OF HETEROPHOS IN WATER, SOIL AND VEGETABLES BY THIN LAYER CHROMATOGRAPHY

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 8, 1977 pp 20-21

KRASNYUKH, A. A., All-Russian Scientific Research Institute for Plant Protection

[Abstract] A simple and sensitive method is suggested for the determination of heterophos residues in water, soil and vegetables (potatoes, onions, etc.). It is based on extraction of the pesticide from the object being studied with hexane and thin layer chromatography of the extracts on types KSK silica gel. For additional purification of the extracts, 2-dimensional chromatography used: the first mobile phase is benzene, the second is chloroform. An aqueous-acetone mixture of bromophenol blue and silver nitrate is used as the developing reagent. The method suggested can be used to study the dynamics of elimination of heterophos residues in water and soil, and also to test for the content of the pesticide in vegetable products.

USSR

UDC 543.8:543.52:546.18:546.13:546.14

SIMULTANEOUS DETERMINATION OF PHOSPHORUS, CHLORINE AND BROMINE IN ORGANO-PHOSPHORUS COMPOUNDS BY USING IRRADIATION WITH FAST NEUTRONS

Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 32 No 6, Jun 77 pp 1214-1216

LISOVSKIY, I. P., and SMAKHTIN, L. A., Branch of the Physicochemical Institute imeni L. Ya. Karpov

[Abstract] A method was developed for the simultaneous determination of phosphorus, chlorine and bromine in different classes of organophosphorus compounds by activation with fast neutrons. The specimens were irradiated near the target of an NG-150M neutron generator with a maximum neutron yield of  $2 \cdot 10^{11}$  neutrons/sec. A lower neutron flux was used in the present study:  $(2-4) \cdot 10^{10}$  neutrons/sec. Test specimens were placed in stainless steel hermetic ampules,  $1.5 \text{ cm}^3$  in interior volume. The following analytical isotopes were found best in the simultaneous determination of these elements: for phosphorus,  $^{28}\text{Al}$  ( $T_{1/2} = 2.3 \text{ min}$ ,  $E_{\gamma} = 1.78 \text{ MeV}$ ); for chlorine,  $^{37}\text{S}$  ( $T_{1/2} = 5.1 \text{ min}$ ,  $E_{\gamma} = 3.1 \text{ MeV}$ ) and for bromine,  $^{78}\text{Br}$  ( $T_{1/2} = 6.5 \text{ min}$ ,  $E_{\gamma} = 0.5 \text{ MeV}$ ). The total analysis time for a single specimen was not more than 15-18 min. The reproducibility of the analytical results obtained by each averaging of three parallel determinations is characterized by a relative standard deviation as follows: in the determination of bromine (0.015-0.02), chlorine and phosphorus (0.02-0.03). The determination limit for them, determined according to the three-sigma criterion, is  $(2-3) \cdot 10^{-3} \text{ g}$ . References 5 (Russian).

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Environmental Pollution

USSR

UDC 628.315.3+628.33(--198.6)

FURTHER PURIFICATION OF BIOLOGICALLY PURIFIED WASTE WATER BY RADIAL FILTER PROCESSING

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 7, 1977 pp 8-10

FOMINIKH, A. M., VOITOV, YE. L., Novosibirsk Construction Engineering Institute imeni V. V. Kuybishev

[Abstract] The Novosibirsk Construction Engineering Institute imeni V. V. Kuybishev has developed a new filter design--a radial filter, intended for further purification of municipal sewage following biological purification. The radial filter consists of a circular filter body of monolithic reinforced concrete having an external barrier made of porous concrete or slit screens of wire with trapezoidal cross sections of brass, stainless steel or steel-copper alloy. The filtering material consists of calcined gangue from a Kuznets Basin coal mine. Water is filtered in from the outside and withdrawn from the center of the circular filter. Studies have shown that the radial filter is an effective, economical and easy-to-use method of further purification of municipal sewage, which can be used in the open.

USSR

UDC 628.52/53:502

A COMBINATION OF MEASURES FOR THE PROTECTION OF THE ENVIRONMENT UNDERTAKEN AT THE NOVOMOSKOVSKIY "AZOT" PRODUCTION UNION

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 7, 1977 pp 6-8

INSHENERI, A. M., Novomoskovskkhimstroi Trust and MOZHAYEV, V. V., Press Center of USSR Industrial Construction Ministry

[Abstract] "Azot" Union, a leading enterprise in its branch, by improving technological processes, replacement of obsolete equipment, improving technological and production discipline and maintaining constant operator control to be sure the norms for raw material and product losses are met, has reduced such losses by a factor of more than 2.5 in comparison to the norms and better than halved its emissions into the atmosphere over the past 10 years, in spite of the fact that new production facilities were put on stream during the Ninth Five-Year Plan. Protection of the environment follows two paths in this union: reduction of the consumption of water and of the loss of raw material and products with waste water and gases, and the construction of new water and gas purification installations. A number of examples of individual measures, such as recovery of organic impurities, collection of waste water and condensate for recycling (20 water recycling systems are in use in all in the union), and the increased use of settling ponds, are presented. Old chemical production shops have been closed down and replaced by new ones utilizing technologies which are less polluting. Each year, a

combined plan for increasing the effectiveness of production is generated at the union, including pollution-control measures.

USSR

PROTECTION OF THE AIR--AN IMPORTANT JOB

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 7, 1977 p 5

UNSIGNED

[Abstract] An important part of the work of improving the condition of labor and daily life of the Soviet people, as stated by L. I. Brezhnev at the 16th Congress of Unions, is preservation of the environment, including prevention of air, water and soil pollution. Intensive development of industry, transportation and construction has resulted in air pollution of industrial enterprises and cities. Many industries are working on methods for predicting air pollution and preventing harmful results. One method is mathematical simulation of pollution in combination with modern methods and devices for purification of air to remove dust and harmful gases before they are emitted into the atmosphere. Nevertheless, pollution control is lagging behind industrial development. Progressive methods of stack gas purification and ventilation of industrial areas are being slowly introduced. Ventilation technology must meet important challenges, so that harmful gases and dust from production areas are vented without polluting the surrounding air. Equipment for testing and control of ventilation and air purification systems should be mass produced.

USSR

UDC 628.11:614.7.001.5

DEVELOPMENT OF STUDIES ON THE CONSERVATION AND EFFICIENT UTILIZATION OF WATER RESOURCES

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 7, 1977 pp 2-4

VASIL'YEV, YU. S., KUDRYASHEV, V. V., Leningrad Polytechnical Institute

[Abstract] This is a report on the republic scientific and technical conference "Man and the Environment." Problems of conservation and efficient utilization of natural resources." The RSFSR Ministry of Higher Education, Academy of Sciences, State Planning Commission, and Many Branch Ministries are included. At the conference the interaction of man and the environment, the need to change traditional ways of thinking concerning more complete utilization of water resources and conservation of the environment were

discussed. The plan to transfer a portion of the discharge of Siberian rivers over an artificial river 2,500 km in length to central Asia and Kazakhstan will involve the transfer of 25 km<sup>3</sup> of water initially, eventually rising to 50 km<sup>3</sup> of water per year, basically changing the hydrographic picture and environment of the two regions. Other problems discussed included the slow rates of biological processes and, therefore, recovery from environmental damage in the far north, protection of water from pollution and purification of polluted water, purification methods utilizing ferrochrome slag and ion exchange, production of steam or condensate from industrial waste water, and protection of bodies of water from detergent pollution, membrane water purification technology, water quality prediction, water recycling and blue-green algae control.

USSR

UDC 613.632.4:547.211+613.633):622.33

HYGIENIC EVALUATION OF NEW TECHNOLOGY FOR CONTROL OF METHANE AND DUST IN COAL MINES

Moscow GIGIYENA I SANITARIYA in Russian No 7, Jul 77 manuscript received 19 Jul 76 pp 24-26

GADZHIEV, G. P., DEYNEGA, V. G., SUKHANOV, V. V., LEVSHINA, I. M., YARYM, N. T., and PETRENKO, G. A., Donets Scientific Research Institute of Labor Hygiene and Occupational Diseases; Moscow Mining Institute

[Abstract] Exploitation of available new technology for mining is hindered by the dangers of gas evolution, and the need for maintenance of hygienic standards. The Moscow Mining Institute has developed, and proposed for industrial introduction, a new process for control of methane and dust in mine shafts; the method will help to raise significantly the productivity of excavating machines in high gas factor shafts. The process to combat methane and dust consists essentially in drilling boreholes from the side of the gallery, or from the outer surface, into the coal-bearing stratum. These boreholes are injected with a 24% solution of urea-formaldehyde resin (binder M<sub>2</sub>), with 1% solution of ammonium chloride hardener. After several months this plastic is removed. This new technology involves the escape of toxic substances into the shaft air. Hence the need for hygienic testing. Additional study must estimate the danger of accidents, e.g., shaft fires, toxicity of combustion products of coal or binder. Study is also needed on pathologies which might occur to miners engaged in removal of the plastic with the new technology. No references.

USSR

UDC 613:633.1

A HYGIENIC EVALUATION OF THE INSECTICIDE RATING SYSTEM

Moscow GIGIYENA I SANITARIYA in Russian No 8, 1977 pp 45-48

PIVOVAROV, YU. P., Prof, IVASHINA, S. A., Candidate in Biological Sciences, and PODALKIN, V. P., Candidate in Medical Sciences, Second Moscow Medical Institute imeni Pirogov, All-Union Scientific-Research Biotechnical Institute, Moscow

[Abstract] The increasingly intensive use of microorganisms in the industrial production of insecticides, pharmaceuticals and other products presents serious possibilities of new hazards to public health and to the environment. Unfortunately, information in this area is limited, and the available information has not been systematized.

The authors recognize three aspects of this general problem: 1) the assurance of a quality of bacteria-produced products which will offer safeguards to public health and the prevention of environmental contamination, along with the corresponding production techniques; 2) the hygienic standardization of preparations produced with the help of microorganisms; this is an especially critical area, in view of the fact that presently accepted methods of standardization are not acceptable for the establishment of maximal permissible concentrations of harmful substances; and 3) the study of the medical consequences of the use of such preparations, and their effect on local ecological structures at production sites. A brief survey of the productive capacities of certain bacterial cultures is given. Reference 1 (Russian).

USSR

UDC 614.777(282.251.1)Tom'

A HYGIENIC EVALUATION OF THE EFFECTIVENESS OF CURRENT MEASURES FOR PREVENTION OF THE POLLUTION OF THE TOM' RIVER

Moscow GIGIYENA I SANITARIYA in Russian No 8, 1977 pp 19-22

SAVELOVA, V. A., KOVTUN, V. P., and BELOZERTSEV, I. I., Moscow Scientific-Research Institute imeni Erisman, Kemerovo Medical Institute, and Kemerovskaya Oblast Sanitation and Epidemic Station

[Abstract] Anti-pollution measures for the Tom' Basin (within the Kemerovo Industrial Network, and also for industrial regions lying upstream) have been taken for many years. Recently they have been greatly intensified. During the period 1970 through 1975, more than 82 million rubles were invested in this effort.

The positive results for this 6-year period show that all forms of pollution decreased by 50% or more, with only sporadic increases. The authors recommend

a combination of calculation and analytical control. Their data in this study are based on direct measurements at selected sites. Some hydrological data on the Tom' River and a computation formula are included.

USSR

UDC 614.777:628.1]-037

THE PREDICTION OF THE SANITARY CONDITIONS OF WATER USE BY THE POPULATION OF NEW ECONOMIC AREAS (ON THE EXAMPLE OF THE CENTRAL SECTION OF THE BAYKAL-AMUR MAIN RAIL LINE)

Moscow GIGIYENA I SANITARIYA in Russian No 8, 1977 pp 11-15

GUREVICH, L. S. and NOVIKOV, YU. V., Doctors of medical sciences, PLITMAN, S. I., Candidate in Medical Sciences, LASTOCHKINA, K. O., Candidate in Biological Sciences, AYZEN, M. S. and YERSHOVA, T. N., Candidates in medical sciences, YEKHINA, R. S. and MIREKIN, V. A., Moscow Scientific-Research Institute of Hygiene imeni Erisman

[Abstract] An analysis is made of the material from a combined study of water-supply sources in the developing regions of Amurskaya Oblast. Results of sanitary-chemical and sanitary-microbiological research have now made it possible to distinguish the roles of both natural and anthropogenic factors in the formation of the quality of water from underground and surface sources in use for domestic and drinking water supply in this region. Some methodological approaches to the prediction of sanitary conditions of water use are formulated, with due allowance for the natural situation in the Amur Region and for existing industrial plans. References 3 (Russian).

USSR

UDC 614.72:546.17-31

THE TRANSFORMATION OF NITROGEN OXIDES IN THE ATMOSPHERE

Moscow GIGIYENA I SANITARIYA in Russian No 8, 1977 pp 8-11

DMITRIYEV, M. T., Doctor of Chemical Sciences, GUBERNSKIY, YU., Candidate in medical sciences, and KLEBANOVA, V. A., Institute of General and Communal Hygiene imeni Sysin, Academy of Medical Sciences USSR, Moscow

[Abstract] Since any air pollutant may experience chemical transformation in the atmosphere, it is not safe to depend on a fixed figure for maximum permissible concentration (MPC) of the primary pollutant when its dispersal is being calculated. To do so may lead to substantial errors in calculating the optimal height of chimneys, the frequency of air exchange in various types

of buildings, the degree of dilution of waste water, and so forth. The authors propose algebraic equations which allow for the amount of the initial pollutant, the amounts of new substances formed as a result of its chemical transformation, and the various factors in the atmosphere which will affect the ultimate dispersal. These equations are then developed to form a system of differential equations whose solution will determine the time variation in the concentrations of various substances involved in transformation. The case of nitric oxide is considered in detail. The errors of proceeding from published MPC for NO and  $\text{NO}_2$  without allowance for the action of physical, chemical and biological factors which may be present, are demonstrated. The proposed method of determining pollutant dispersal is based upon well-known mathematical procedures, and is adaptable to computer techniques. References 9: 7 Russian, 2 Western.

USSR

UDC 628.356

MATHEMATICAL MODEL OF THE PROCESS OF BIOLOGICAL PURIFICATION ON FLOCCULES OF ACTIVE SILT

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 233 No 5, 1977 pp 922-925  
manuscript received 2 November 76

VAVILIN, V. A., and VASIL'YEV, V. B., Institute of Water Problems, Academy of Sciences USSR

[Abstract] A model is presented which describes the kinetics of biological purification of sewage include three variables, the processes of biochemical oxidation of organic matter, and the effect of sorption by active silt. The model may be used to design aerotank active silt regenerator systems. Calculations show that the regenerator is particularly effective for aerotank extractors, which assure deep purification of sewage. References 3 (Russian).

## Fertilizers

USSR

UDC 631.82:633.11:631.559:631.445.4(470.324)

CHANGES IN WINTER WHEAT GRAIN QUALITY AS A RESULT OF FERTILIZERS ON LEACHED CHERNOZEM SOILS IN VORONEZH OBLAST'

Moscow AGROKHIMIYA in Russian No 6, 1977 pp 66-70 manuscript received 23 Jun 1976

PRESNYAKOV, N. A., and GRIDYAYEVA, L. I., Voronezh Agriculture Institute

[Abstract] The effects of varying regimes of nitrogen, phosphorus and potassium fertilizers on protein accumulation were studied, with specific attention to stages of plant maturation at the time of fertilization. Mironovskaya 808 winter wheat variety was planted in 1972-1974, in rotation after sainfoin. Production conditions of planting and cultivation and harvesting were maintained. The basic fertilizer was  $N_{aa}$  (34%),  $P_{cr}$  (19.2%), and  $K_x$  (60%), with additional  $N_m$  (46%). Meteorological conditions varied widely during the test period. Increments from phosphorus and potassium applied at planting were statistically insignificant, but nitrogen increased protein and fiber content. In wet years nitrogen and phosphorus helped prevent stalk collapse thus permitting better irrigation. Results showed that mineral fertilizers were effective after the stage of milky ripeness of winter wheat grain. In early grain development they did not affect storage of albumin and globulins, but gliadins and glutinins increased. This also occurred at full ripening, so that a dosage of N60P60K60 appeared to be optimal with a spring additional fertilization of N30. References 13 (Russian).

USSR

UDC 631.82:631.524.28:633.15

FERTILIZING AND THE DEGREE OF CORN DENSITY

Moscow AGROKHIMIYA in Russian No 4, Apr 77 pp 64-68 manuscript received 3 May 76

VITRIKHOVSKIY, P. I., IVASHCHENKO, A. V., LEVITSKIY, G. P., POPOVICH, I. A., ROMANENKO, L. G., and STRYUK, M. V., Ukrainian Scientific-Research Institute of Agriculture, Kievskaya Oblast; Zhitomirskaya, Zakarpatskaya, Ternopol'skaya, and Khmel'nitskaya Experimental Stations

[Abstract] Study of the influence of fertilizers on the yield of grain and silage corn under conditions of sufficient moistening of the western Lesostep' (Forest Steppe region), Poles'ye, and Transcarpathia, has shown that the optimum dose of nitrogen against a background of P120K120 equals 150-180 kg/hectare. For more efficient utilization of such fertilizer doses it becomes necessary to increase the number of plants in comparison with the number recommended for 5-10 thousand per hectare. Thus, the conducted experiments confirm the necessity of some increase in the density of corn-plant planting

with the application of increased fertilizer doses. This agrees with previously conducted research. Tables 4; references 14: 11 Russian, 2 Polish, 1 Roumanian.

USSR

UDC 631.82:633.11

EFFECT OF MINERAL FERTILIZERS ON THE YIELD OF WINTER WHEAT AS A FUNCTION OF SEEDING RATE AND VARIETY

Moscow AGROKHIMIYA in Russian No 4, Apr 77 pp 57=63 manuscript received 1 Apr 76

GOL'TSEVA, O. F., Odessa Agricultural Experimental Station

[Abstract] In studies conducted in 1972-1974 in the Odessa region, it was ascertained that on southern low-humus chernozems the harvest and quality of winter wheat on black fallows depends upon the sowing norms, the variety, and the applied fertilizers. On unfertilized black fallows the harvest increased with an increase of the sowing norm from 3 to 6 million seeds per hectare. The sowing norm of 3 to 4 million seeds per hectare was more efficient with the application of fertilizers. Different varieties require a different background of fertilizers. Tables 4.

USSR

UDC 631.84:631.874.3:633.18

PRODUCTIVITY OF RICE IN RELATION TO DOSES OF NITROGENOUS FERTILIZERS AGAINST A BACKGROUND OF GREEN MASS AND STUBBLE REMAINS OF INTERMEDIATE CROPS

Moscow AGROKHIMIYA in Russian No 4, Apr 77 pp 27-31 manuscript received 29 May 76

RAVSHANOV, A. and SHASHCHENKO, V. F., All-Union Scientific Research Institute of Rice

[Abstract] In an attempt to determine the optimum doses of nitrogenous fertilizers under rice against a background of green mass and stubble remains of intermediate crops for obtaining the maximum rice harvest, field experiments on the meadow- and chernozem-type soils of Krasnodarskiy kray have ascertained that optimum doses of nitrogen under rice respectively comprised 90 and 120 kg/hectare with the plowing in of 418 and 346 centners of green mass of intermediate crops, and 150 kg/hectare against a background of stubble and root remainders of these crops. Figure 1; tables 2; references 3 (Russian).

USSR

UDC 631.841:633.18:631.67

THE EFFECT OF CYANGUANADINE UPON THE DYNAMICS OF AMMONIUM IN THE SOIL AND NITROGEN ASSIMILATION BY RICE AT VARIOUS IRRIGATION MODES

Moscow AGROKHIMIYA in Russian No 4, Apr 77 pp 22-26 manuscript received 5 Apr 76

KUDEYAROV, V. N., STREKOZOVA, V. I., and TUR, N. S., Institute of Agrochemistry and Soil Science, Academy of Sciences, All-Union Scientific Research Institute of Rice

[Abstract] In a vegetation experiment during research conducted with rice at an experimental base of the All-Union Scientific Research Institute of Rice at Krasnodarskiy kray, the combined application of cyanguanidine with ammonium sulfate at two aqueous modes (100% maximum field-moisture soil capacity and a water layer) facilitated a decrease in the immobilization of ammoniacal nitrogen. Reliable rice-grain yield increments due to cyanguanidine have been obtained against an NPK background. Figures 2; tables 2; references 17: 10 Western, 7 Russian.

USSR

UDC 631.84:633.11(477)

THE INFLUENCE OF THE FREQUENCY AND METHODS OF APPLICATION OF NITROGEN FERTILIZERS ON THE GRAIN QUALITY OF WINTER WHEAT IN THE UKRAINIAN STEPPE

Moscow AGROKHIMIYA in Russian No 4, Apr 77 pp 17-21 manuscript received 24 May 76

MAKAROVA, A. YA., and ZHEMELA, G. P., All-Union Scientific Research Institute of Corn

[Abstract] In field experiments on ordinary chernozem conducted at an experimental farm of the All-Union Scientific Research Institute of Corn, winter-wheat grain quality was best when nonroot supplementary feedings were carried out in the period after heading prior to commencement of milk-ripeness of the grain, soil-surface supplementary feeding being effective only in years with sufficient precipitation. Tables 3; references 10 (Russian).

## Nitrogen Compounds

USSR

UDC 547.779:542.943

### N-ANIONS OF HETEROAROMATIC AMINES. VII. AUTOXIDATION OF N-ANIONS OF 3-AMINOINDAZOLES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY No 7, Jul 77 pp 952-955 manuscript received 2 Nov 76

FILIPSKIKH, T. P., and POZHARSKIY, A. F., Rostov State University

[Abstract] Some years ago one of the authors discovered the ability of poly-N-anions of 2-aminobenzimidazoles to undergo autoxidation under unusually mild conditions (liquid ammonia) to form 2,2'-azo- and 2-nitrobenzimidazoles. In this work, the authors are attempted to extend this reaction to 3-aminoindazoles, which are isomers of 2-aminobenzimidazoles. Their studies show that N-anions of 3-aminoindazoles, like the N-anions of 2-aminobenzimidazoles, are easily subjected to autoxidation. However, in contrast to the 2-aminobenzimidazoles, they do not form nitrosocompounds, but in certain cases are converted to azoxycompounds, the formation of which was not observed in the 2-aminobenzimidazole series. References 10: 5 Russian, 5 Western.

USSR

UDC 547.754.83

### FORMATION OF 3,4-DIHYDRO- $\alpha$ -CARBOLINES from 2-MINOINDOLE

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY No 7, Jul 77 pp 945-951 manuscript received 5 Dec 76

SAGITULLIN, R. S., KOST, A. N., MELNIKOVA, T. V., and SHARBATYAN, P. A., Moscow State University

[Abstract] The authors condensed 2-aminoindole hydrochloride with various  $\alpha,\beta$ -unsaturated ketones and aldehydes. The reaction was performed in isopropyl alcohol with the addition of excess triethylamine. Under these conditions, ethylidene acetone, crotonic aldehyde and methyl vinyl ketone produced 2,4-dimethyl-, 4-methyl- and 2-methyl- $\alpha$ -carbolines, i.e., the carbon atom of the double bond of the unsaturated oxo compound interacts with the  $\beta$  position of the aminoindole. The compounds produced were colorless substances with strong fluorescence in UV light characteristic for  $\alpha$ -carbolines. The combination of spectral characteristics of the dihydro structures and their oxidation to the corresponding  $\alpha$ -carbolines yields an unambiguous answer concerning the structure of  $\alpha$ -carbolines formed from unsaturated oxo compounds. References 16: 5 Russian, 11 Western.

USSR

UDC 547.759,3'5.07:541.63:543.422.25.4.6

PYRROLOINDOLES. 1. SYNTHESIS OF 1H, 6H-PYRROLO [2, 3-e]INDOLE

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 7, Jul 77 pp 938-944 manuscript received 17 Nov 76

SAMCONIYA, SH. A., TARGAMADZE, N. L., TRET'YAKOVA, L. G., YEFIMOVA, T. K., TURCHIN, K. F., GVERDTSITELI, I. M., and SUVOROV, N. N., Moscow Chemico-Technological Institute imeni D. I. Mendeleyev

[Abstract] Earlier papers have reported the synthesis of pyrroloindole derivatives, but none have yet succeeded in producing a quantity of the unsubstituted heterocycle sufficient to study its physical-chemical properties. The authors of this report produced 1H, 6H-pyrrolo[2,3-e]indole by Fisher cyclization of m-phenylenedihydrazone of pyruvic acid and the ethyl ester of pyruvic acid, using hydrogen sulfide to eliminate the tin salts and separating the dihydrazine base with sodium acetate. The reaction can be conducted in an acid medium with relatively good yield (40-70%). The physical properties of the syn and anti forms of the hydrazones are described, and UV and IR spectral curves are presented. References 11: 3 Russian, 8 Western.

USSR

UDC 547.758.7'759

ARYL-(7-INDOLYSYL)METHANES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 5, 1977 pp 646-649

PROSTAKOV, N. S., KUZNETSOV, V. I., SAVINA, A. A., RYASHENTSEVA, M. A., and ZVOLINSKIY, V. P., University of the Friendship of Peoples imeni Patrice Lumumba

[Abstract] Quaternization of aryl(gamma-pyridyl)methanes with bromoacetophenone, followed by cyclization of the quaternary salts with 40 percent potash yielded aryl(6-methyl-2-phenylindolyl-7)methanes (Chichibabin's method). When the corresponding quaternary salt was treated with a 10 percent potash solution, the stable benzoylmethylide of 2-5-dimethyl-4-(2,4-dimethylbenzyl)-pyridinium was isolated; treated with Al<sub>2</sub>O<sub>3</sub>, it was converted into indolysine. From paramagnetic resonance spectra, 3-unsubstituted indolysines were shown to be protonatable at not only the 3-position, but also the 1-position. Aryl(7-indolysyl)methanes selectively hydrogenate over rhenium heptasulfide at the indolysine ring to the tetra- or octahydro-derivatives without involving the aryl groups. Infrared, paramagnetic resonance and mass spectral data are presented. References 7: 4 Russian, 3 Western.

USSR

UDC 543.51:547.759.3'853

MASS SPECTRA OF 2,3,4,5-TETRAHYDROPRIMIDO[3,4-ALPHA]INDOLES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 5, 1977 pp 650-652

BELIKOV, A. B., TERENT'YEV, P. B., and BORISOVA, L. N., Institute of Pharmacology and Chemotherapy, USSR Academy of Medical Sciences, and Moscow State University imeni M. V. Lomonosov

[Abstract] Under electronic bombardment, dissociative ionization of substituted 2,3,4,5-tetrahydropyrimido[3,4-alpha]indoles occurs in two directions. The first direction is the elimination of the  $R_1NCHR_2$  group when  $R_1$  is  $CH_3$ . The second direction, typical of compounds that have the formyl substituent ( $R_1$  is  $CHO$ ) or have no substituent ( $R_1$  is  $H$ ) at the amine nitrogen, is the cleavage of the  $CH_2NCHR_2$  group, with the migration of the amino-group hydrogen to the fragmental ion; this was confirmed by the spectrum of the deuterium-labeled compound. The principal peaks of ions, cleavage and rearrangement, together with the molecular ion in the mass spectra account for 55.0-70.0 percent in the complete ion beam. Present in the mass spectra are ion peaks characterizing the presence of a methoxy group and chlorine in the indole part of the molecule. Ion compositions were confirmed by high-resolution mass spectra. References 4: 3 Russian, 1 Western.

Organometallic Compounds

USSR

UDC 539.69:539.143.43:547.26.119

SYNTHESIS AND NMR  $^1\text{H}$  SPECTRA OF ESTERS AND AMIDOESTERS OF ARSONIC ACIDS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 47(109) No 6, Jun 77 pp 1285-1288

GAMAYUROVA, V. S., DAYNEKO, Z. G., MOROZOVA, N. K., and CHERNOKAL'SKIY, B. D., Kazan' Chemical Technology Institute imeni S. M. Kirov, and Volgograd Polytechnic Institute

[Abstract] Previously unreported compounds of tetra-coordinated arsenic were synthesized and investigated: esters and amidoesters of aronic acids. Their paramagnetic resonance spectra were studied in comparison with the spectra of other organoarsenic derivatives. Chemical shifts of methylene protons at the arsenyl group in esters of aronic acids are somewhat displaced toward the side of the weak field compared with analogous characteristics of amidoesters of aronic acids. Apparently, this can be explained by the electron-donor influence of the amido group. Analysis of chemical shifts of fragments associated with the arsenic atom indicates the descreening influence of the arsenyl group. References 8: 4 Russian, 4 Western.

USSR

UDC 547.242

SYNTHESIS OF SOME DERIVATIVES OF 5,10-DIHYDROPHENARSINE

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 47(109) No 6, Jun 77 pp 1282-1285

GAVRILOV, V. I., TIKTINSKIY, V. B., KHRUSHCHEVA, G. A., and CHERNOKAL'SKIY, B. D., Kazan' Chemical Technology Institute imeni S. M. Kirov

[Abstract] Derivatives of 5,10-dihydrophenarsine are valuable as active constituents of nonfouling paints and in the study of  $d_{\text{pi}}\text{-}p_{\text{pi}}$  interaction with the participation of the arsenic atom. New representatives of this class of compounds were prepared. 10-Aryl-5,10-dihydrophenarsines were synthesized by the reaction of tetrahydrofuran solutions of the corresponding organomagnesium compounds with 10-chloro-5,10-dihydrophenarsine. The following representatives of 5,10-dihydrophenarsine were prepared: 10-m-anisyl-, 10-m-fluoro-phenyl-, 10-p-trifluoromethyl-phenyl-, 10-m-chlorophenyl-, 10-m-tollyl-, 10-p-allylphenyl-, 10-p-bromophenyl-, and 10-m-dimethylaminophenyl-5,10-dihydrophenarsines. By oxidation of the corresponding arsines with hydrogen peroxide, the oxides of 10-m-dimethylaminophenyl-, 10-m-chlorophenyl- and 10-p-bromophenyl-5,10-dihydrophenarsazines were prepared. References 9: 4 Russian, 5 Western.

USSR

UDC 547.242+538.27

CORRELATION OF ABSOLUTE CONFIGURATION OF CHIRAL SULFIDES OF TERTIARY ARSINES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1276-1282

IONOV, L. B., SAMITOV, YU. YU., KOKORINA, L. G., KOROVYAKOV, A. P., and CHERNOKAL'SKIY, B. D., Udmurt State University, and Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] Enantiomeric purity and absolute configuration of the active sulfides of tertiary arsines was the reason for a study of halogen anhydrides of alkylarylthioarsinic acids in facile reaction with mentholides of alkali metals or with menthol in the presence of pyridine, forming a mixture of diastereoisomers of the menthyl ester of the corresponding thioarsinic acid. In preparing diastereo-isomers of menthyl esters of asymmetric thioarsinic acids, it is convenient to start from the corresponding acid chlorides of acids and sodium mentholide. The reaction of diastereo-isomers of menthyl esters of ethylphenylthioarsinic acids with Grignard reagents and alkyl-lithium is a two-stage process, proceeding with the inversion of configuration and with a high degree of stereo-specificity. Optical stability of the resulting enantiomers of ethylpropylphenylarsine was demonstrated. References 10: 4 Russian, 6 Western.

Organophosphorus Compounds

USSR

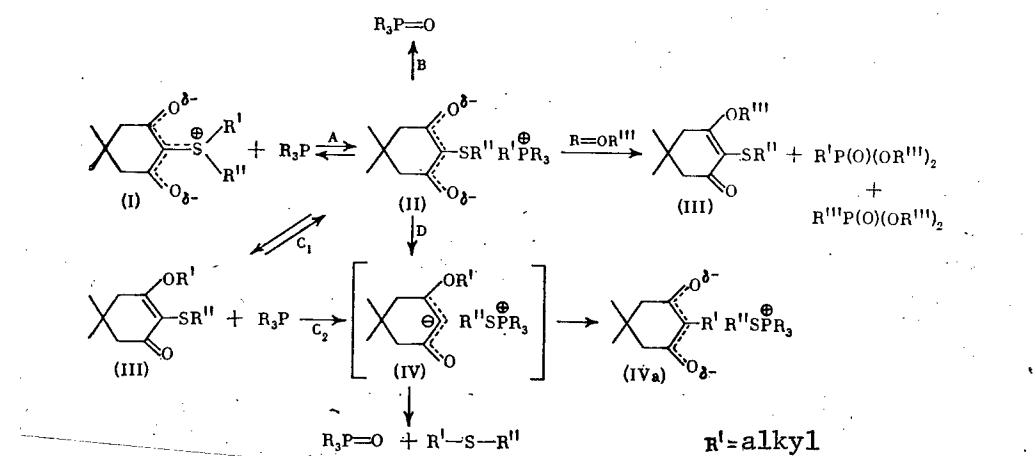
UDC 542.91:547.379.2+547.341+547.26'118

NONCLASSICAL ARBUSOV REARRANGEMENT. COURSE OF REACTION OF CARBONYL-STABILIZED SULFONIUM YLIDES WITH TRIVALENT PHOSPHORUS DERIVATIVES

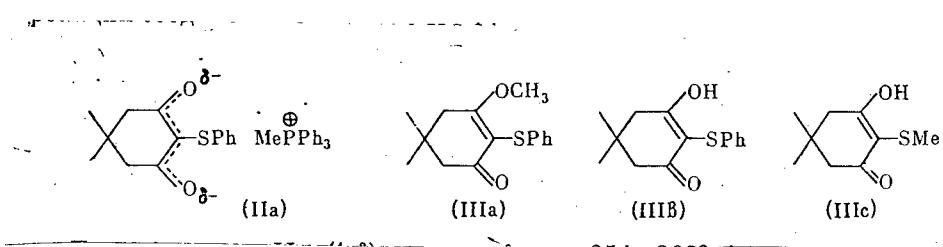
Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 236 No 1, Sep 77 manuscript received 26 May 77 pp 95-98

BELKIN, YU. V., POLEZHAYEVA, N. A., and ARBUZOV, B. A., Scientific Research Chemistry Institute imeni A. M. Butlerov, Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] The title institute has shown that carbonyl-stabilized sulfonium ylides (CSY) (see I in following series of reactions) react with triphenylphosphine (TPP) and tris-(dimethylamino)-phosphine (TDMAP) to form oxides, thioxides of TPP and TDMAP, sulfides, and phosphinic salts; CSY reacts with trialkylphosphites (TAP), to form alkylphosphonates, 2-phenylthio-3-alkoxy-5,5-dimethylcyclohexene-2-one (see III in the following series), and trialkylphosphates. It is possible that the resulting phosphinic salts, stabilized by an enolate ion (see II), are intermediate products which break down:



It is suggested that breakdown of II salts may proceed in several ways: path A (above) yields the sulfonium ylide I and a derivative of trivalent phosphorus (DTP), but under reaction conditions I reacts with the latter to regenerate II; path B should form an oxide of DTP; path C—reaction of an oxygen atom with carbon of the R-alkyl group—yields III and DTP which, via the unstable intermediate IV, forms the products seen. Salt IV can proceed directly from II by a nucleophilic attack of the sulfur atom on the phosphorus atom with simultaneous migration of the R-alkyl group from the phosphorus atom to the oxygen of the enolate ion, i.e., path D. Confirmation of the breakdown paths suggested has been undertaken by study of thermolysis of methyltriphenylphosphonium of 2-phenylsulfenyldimedone (IIa), and reactions of compounds of type III with DTP.



Conditions of reactions and the identifying physical and chemical properties of products obtained are given. Data not only support the suggested scheme of reaction of CSY and DTP, but also permit prediction of the nature of the products which will form. References 10: 4 Russian, 6 Western.

USSR

UDC 661.719

## METHODS OF SYNTHESIZING THE MIDDLE ESTERS OF DISELENOPHOSPHORIC ACID; SOME OF THEIR PROPERTIES

KIEV UKRAINSKIY KHMICHESKIY ZHURNAL in Russian No 7, 1977 pp 721-724

KOLODIY, YA. I., MEL'NIK, YA. I., ZEMLYANSKIY, N. I., and TURKEVICH, V. V.,  
Lvov State University imeni I. Franko

[Abstract] Until recently (1973), the only known method of obtaining the middle diselenophosphoric acid esters was based on alkylation of the potassium salts of the 0,0-dialkyldiselenophosphoric acid group, using haloid alkyls. A new method is based on the reaction between elementary selenium and the middle esters of selenophosphoric acid, and on the interaction of dialkylselenophosphoric acid chlorides with selenyls in the presence of a base. The reaction of dialkylchlorophosphites with phenylselenol in the presence of triethylamine was used for the first time to obtain the middle esters of selenophosphoric acid. The structure of the substances obtained was confirmed by chemical transformations, infrared spectra and elementary analysis. Procedures are given for producing five of these esters, along with tables of physicochemical data for most of them. References 5: 4 Russian, 1 Western.

USSR

UDC 547.341

SYNTHESIS OF HEXACOORDINATED COMPOUNDS OF PHOSPHORUS

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1432-1433

VOZNESENSKAYA, A. KH., RAZUMOVA, N. A., PETROV, A. A., and SHEPTIYENKO, O. G., Leningrad Technological Institute imeni Lensovet

[Abstract] A study was made of reactions of 2-diethylamino-2,2-(4,5-dimethyl)-ethylenedioxy-5-methyl-4-isoxaphospholine and 2-diethylamido(2,2-ethylene-dioxi)-5-methyl-4-isoxaphospholine with pyrocatechin; it was found that when pyrocatechin acts on spirophosphoranes containing the P-NR<sub>2</sub> group, hexacoordinated pentahydroxypyrophosphoranes containing five P-O bonds and one P-C bond are obtained. References 2: 1 Russian, 1 Western.

USSR

UDC 541.67:547.241

CONTACT CONTRIBUTION TO LANTHANIDE SHIFTS OF <sup>1</sup>H AND <sup>31</sup>P IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF PHOSPHONATES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1431-1432

BERKOVA, G. A., ZAKHAROV, V. I., SMIRNOV, S. A., MORKOVIN, N. V., and IONIN, B. I., Leningrad Technological Institute imeni Lensovet

[Abstract] By comparing lanthanide shifts of protons in several phosphonates induced by complexes of praseodymium and europium with heptafluorodimethyl-octanedione Pr (fod)<sub>3</sub> and Eu (fod)<sub>3</sub>, it was found that the ratios of these shifts  $\Delta$ Pr/ $\Delta$ Eu for nuclei closest to the coordination center and distant from it afford a more concrete estimation of the fraction of the contact contribution to the lanthanide shift. Limiting lanthanide shifts were obtained for 3-chloro-2-butenediethylphosphonate and 2-chloropropanedimethylphosphonate. The lanthanide shifts of <sup>31</sup>P are much larger in magnitude, differ in sign and depend substantially on substituents at the phosphorus atom. Comparison with proton lanthanide shifts suggests the conclusion that the contact contribution plays a much larger role to the lanthanide shifts of phosphorus. References 5: 1 Russian, 4 Western.

USSR

UDC 547.76.88

ISOMERIZATION OF OXASAPHOSPHOLINES IN DIAZADIPHOSPHANES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 p 1422

GOLOLOBOV, YU. G., and NESTEROVA, L. I., Institute of Organic Chemistry,  
Ukrainian SSR Academy of Sciences

[Abstract] Acted on by triethylamine, esters of N-dichlorophosphino-alpha-alkylaminoacetic acid over a period of several days at 20° without solvent cyclize into previously unreported 1,3,2-oxasaphospholines and 1,4-diaza-2,5-diphosphanes. The phospholines, after subsequent distillations or prolonged storage (5-7 days), are converted into diphosphane. This conversion suggests that diphosphane can be formed not only directly from the esters under the effect of triethylamine, but also by isomerization of phospholines into diphosphane. References 2 (Russian).

USSR

UDC 547.26'118.07+546.185

REACTION OF CHLOROPHOSPHINES WITH CARBONYL DERIVATIVES OF INDOLE

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 p 1421

RAZUMOV, A. I., GUREVICH, P. A., NURTDINOV, S. KH., MUSLIMOV, S. A., and TYL'NOVA, L. M., Kazan' Chemical Technology Institute imeni S. M. Kirov

[Abstract] The reactions of diphenylchlorophosphine with indole-aldehyde and isatin was investigated. The reagents were heated in boiling xylene for 2.5-3 hr. After removal of the solvent, the products were purified by repeated precipitation from acetone solution into water. Hydrolysis of the products with 5 percent HCl yielded the corresponding phosphorylated derivatives of scatole and isatin, unsubstituted at the nitrogen atom. Four products were obtained: 1-diphenylphosphino-3-(chlorodiphenylphosphinoxide)-methylindole; 1-acetyl-3-(chlorodiphenylphosphinoxide)methylindole; 1-diphenylphosphino-3-chloro-3-diphenylphosphinoxide-2-oxindole; and 1-acetyl-3-chloro-3-diphenylphosphinoxide-2-oxindole. References 2 (Russian).

USSR

UDC 547.26'118

O-ALKYLATION OF ALKALI SALTS OF MONOTHIOACIDS OF PHOSPHORUS WITH ALKYLtosylates IN HEXAMETHYLPHOSPHORTRIAMIDE

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 47(109) No 6, Jun 77 p 1420

MASTRYUKOVA, T. A., GENKINA, G. K., KALYANOVA, R. M., SHCHERBINA, T. M., and KABACHNIK, M. I., Institute of Organoelemental Compounds, USSR Academy of Sciences

[Abstract] In the alkylation of alkaline salts of monothioacids of phosphorus with propyl- and isopropyltosylates in hexamethylphosphorthiamide (HMPTA), O-derivatives are formed in large yield, and sometimes predominantly. The experiments were conducted with equimolar amounts of the starting products ( $4 \cdot 10^{-4}$  g-mole) in 25 ml HMPTA at 50-70° for 9-11 hr. Reaction products were diluted with benzene and washed with water in 5 percent HCl from unreacted salt and HMPTA and analyzed by gas-liquid chromatography using reference standard esters of thionic and thiolic structure. Using HMPTA was found, since it is a good cation-solvating agent and an alkylating agent with a good retreating group, alters the direction of alkylating thion-thiol ambidental anions; increasing the basicity of the ambident anion also promotes O-alkylation. References 5: 3 Russian, 2 Western.

USSR

UDC 543.253:547.52

POLAROGRAPHIC STUDY OF SOME PHOSPHORUS-CONTAINING AROMATIC DINITRO COMPOUNDS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 47(109) No 6, Jun 77 pp 1273-1276

NIKOLAYEV, G. N., SAYKINA, M. K., and STAVINCHUK, V. G., Chuvash State University

[Abstract] Since phosphorylated aromatic nitro compounds are used as starting products in dye synthesis, a study was made of the behavior of phosphorus-containing aromatic dinitro compounds on a dropping mercury electrode and a method of their determining their polarographic characteristics was developed. Specifically, the polarographic behavior of the following compounds was studied: di(o-nitrophenyl)ethylphosphonate, di(o-nitrophenyl)heptylphosphonate and di(p-nitrophenyl)ethylphosphonate. These compounds were shown to form on polarograms a single wave corresponding to irreversible reduction with the participation of 12 electrons; diamines are formed in the process. Quantitative determination of these compounds polarographically was shown to be possible. References 9: 5 Russian, 4 Western.

USSR

UDC 547.241+547.78

ESTERS OF IMIDAZOLINYLALKYLPHOSPHONIC AND IMIDAZOLINYLALKYLPHOSPHINIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1270-1273

SHISHKIN, V. YE., ZOTOV, YU. L., and NO, B. I., Volgograd Polytechnic Institute

[Abstract] In a continuation of the study of chemical transformations of phosphorylated iminoesters and the possibility of obtaining compounds with potential biological activity, hydrochlorides of phosphorylated iminoesters--derivatives of phosphonic and phosphinic acids--were brought into reaction with ethylenediamine. Hydrochlorides of esters of omega-imino-omega-alkoxy-alkylphosphonic acids and hydrochlorides of esters of phenyl-omega-imino-omega-alkoxyalkylphosphinic acids react with ethylenediamine, forming esters of imidazolinylalkylphosphonic and imidazolinylalkylphosphinic acids at high yields. Several new phosphorylated imidazolines were obtained. The phosphorylated imidazolines exhibit acaridical activity. References 3; 2 Russian, 1 Western.

USSR

UDC 547.241+253

REDUCTION OF ORGANYLTETRACHLOROPHOSPHORANES WITH ORGANOLITHIUM COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 47(109) No 9, Jun 77 pp  
1267-1270

TIMOKHIN, B. V., DMITRIYEV, V. I., BOYKO, G. A., GRECHKIN, YE. F., and GLUKHIKH, V. I., Institute of Petrochemical and Coal-tar Synthesis at the Irkutsk State University imeni A. A. Zhdanov

[Abstract] In reactions with excess organolithium compounds of aromatic and aliphatic series, phenyltetrachlorophosphorane was found to yield the corresponding tertiary phosphines. Specifically, the reaction of styryltetrachlorophosphorane with phenyllithium formed diphenylstyrylphosphine. Data obtained confirmed an assumption that the reduction and the formation of organic halogenide corresponding to it are observed only when the reaction system includes triorganyldichlorophosphorane. Noted was the anomalous course of the reaction of phenyltetrachlorophosphorane with tert-butyllithium, leading to the corresponding secondary phosphine and phosphonous acid. References 10: 4 Russian, 6 Western.

USSR

UDC 547.241

STRUCTURE OF SALTS OF PHOSPHONIUM AND QUASIPHOSPHONIUM IN SOLUTIONS

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1259-1263

NESTEROV, L. V., ALEKSANDROVA, N. A., TEMYACHEV, I. D., MUSINA, A. A., and  
GAYNULLINA, R. G., Institute of Organic and Physical Chemistry imeni A. Ye.  
Arbuzov, and Kazan' Branch of the USSR Academy of Sciences

[Abstract] Salts of phosphonium and quasiphosphonium were studied by nuclear magnetic resonance of  $^1\text{H}$  and  $^{31}\text{P}$ . Data obtained showed that the chemical shifts of protons in two solvents (methylethyldiisobutoxyphosphonium iodide and methylethyldiisobutoxyphosphonium borofluoride) are different. Formation of the hydrogen bond was found to be affected by solution dilution. Also influencing the hydrogen bond was the relative concentration of the iodide-anion and the quasiphosphonium cation. It was concluded that no covalent halogen-phosphorus bonds are formed in solutions of chlorides, bromides and iodides of phosphonium and quasiphosphonium. In the solutions the halogenide-anions are associated with the quasiphosphonium or phosphonium cations by the formation of hydrogen bonds with alpha-protons of alkyl groups bonded to the phosphorus atoms. References 18: 9 Russian, 9 Western.

USSR

UDC 547.241

REACTION OF SECONDARY CHLOROPHOSPHINES WITH CYCLIC KETONES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1256-1259

NURTDINOV, S. KH., ISMAGILOVA, N. M., ZYKOVA, T. V., SALAKHUTDINOV, R. A.,  
and TSIVUNIN, V. S., Kazan' Chemical Technology Institute imeni S. M. Kirov

[Abstract] Continuing the reactions of trivalent phosphorus with aliphatic ketones in a donor-acceptor reaction scheme, the reaction of secondary chlorophosphines with cyclic ketones was studied. It was found that these components in equimolar amounts react with heating in a closed system for 5-10 hr at 100-200°. The main products of the reaction of diethyl(or phenylethyl) chlorophosphines with cyclohexane, 4-methylcyclohexanone and cyclopentanone are oxides of tertiary phosphines. Figures 2; references 4 (Russian).

USSR

UDC 547.82+541.63

SYNTHESIS OF DIETHYL ESTERS OF CIS- AND TRANS-2-(BETA-PYRIDYL)VINYLPHOSPHONIC ACIDS

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1251-1256

L'VOVA, S. D., KOZLOV, YU. P., and GUNAR, V. I., All-Union Scientific Research Vitamin Institute

[Abstract] Physical-chemical and coenzyme properties of analogs of pyridoxal-5'-phosphate with fixed position of the phosphorus moiety was studied to find the conformation of the 5'-phosphate group in the enzyme and its possible role during catalytic reaction. The possibility of introducing cis- and trans-vinylphosphonic groups at the 5' position of the pyridine ring was investigated with the simplest analog of this series--the ester of 2-(beta-pyridyl)-vinylphosphonic acid. The diethyl ester of cis-2-(beta-pyridyl)vinylphosphonic acid was synthesized by the catalytic hydrogenation of the diethyl ester of beta-pyridylethynylphosphonic acid. The diethyl ester of trans-2-(beta-pyridyl)vinylphosphonic acid is the predominant product of the condensation of beta-formylpyridine with the Li-derivative of the diethyl ester of trimethylsilylmethylphosphonic acid. References 9: 2 Russian, 7 Western.

USSR

UDC 546.185+547.41 2

PROPERTIES AND ANALYSIS OF GAS-LIQUID CHROMATOGRAPHY OF FLUORALKOXY- AND FLUORALKOXYHALOGEN CYCLOPHOSPHAZENES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1247-1251

PRONS, V. N., GRINBLAT, M. P., SHAROV, V. N., and KLEBANSKIY, A. L., All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev

[Abstract] In the preparation of fluoralkoxycyclophosphazenes by the reaction of hexachlorocyclotriphosphazene with sodium alcoholates of fluoro-alcohols in ether or toluene solution, six cyclophosphazenes of differing degrees of substitution may be formed. Analysis of gas-liquid chromatographs of the reaction mixtures showed that by controlling the process conditions (order and rate of addition of reagents, solvent and temperature), the reaction direction does not predominantly favor the formation of any single compound. Since the fluoroalkoxychlorocyclophosphazenes have a narrow spread in boiling points, fixed phases of high selectivity and adequate thermal stability are required in gas-liquid chromatography. The selectivity of the organosilicon phase in the gas-liquid chromatography of fluoroalkoxychlorocyclophosphazenes is determined primarily by the donor-acceptor reaction of chlorine in the cyclophosphazene molecule with the silicon atom in the fixed phase. References 7: 3 Russian, 4 Western.

USSR

UDC 547.241

DIALKOXYPHOSPHINES. V. REACTIONS OF ALKYLATION AND ACYLATION; SYNTHESIS OF ALPHA-KETOPHOSPHONITES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1244-1247

PROSKURNINA, M. V., KARLSTEDT, N. B., and LUTSENKO, I. F., Moscow State University imeni M. V. Lomonosov

[Abstract] Acylation and alkylation of dialkoxyphosphines was studied to develop a more preparative method of synthesizing alpha-ketophosphonites. Sterically hindered alpha-ketophosphonites--dibutylisobutyrylphosphonite and dibutylpivaloylphosphonite--form at yields of 40 and 60 percent, respectively, in the reaction of dialkoxyphosphines with acid chlorides of the corresponding carboxylic acids. Sterically unhindered alpha-acetylphosphonite forms with only a yield of 12 percent. The reaction of dialkoxyphosphines with halogenide derivatives does not proceed via the Arbuzov rearrangement; the primary direction of the process is reduction at the carbon-halogen bond. References 5: 2 Russian, 3 Western.

USSR

UDC 547.26'118

SYNTHESIS OF PHOSPHORYLATED 2-METHYLMIDAZOLINES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp 1242-1244

PROKOF'YEVA, A. F., MEL'NIKOV, N. N., and VLADIMIROVA, I. L., All-Union Scientific Research Institute of Chemical Agents of Plant Protection

[Abstract] To find biologically active compounds, derivatives of thiophosphoric acids containing a five-membered imidazoline ring as the amide group at the phosphorus atom were synthesized. N-[0,0-dialkyl(diaryl)thiophosphoryl]-2-methylimidazolines were prepared by the reaction of acid chlorides of thiophosphoric acids with 2-methylimidazoline in a water-alcohol medium in the presence of alkali at -15 to 20° and at equimolar reagent ratio. The products formed at a 70-90 percent yield; they are liquids distilled in vacuum without decomposition, or crystalline compounds. The phosphorylated 2-methylimidazolines exhibit fungicidal activity. References 4 (Western).

USSR

UDC 547.341

## PHOSPHONYL- AND THIOPHOSPHONYLHETERYLUREAS

Leningrad ZHURNAL OBSCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1238-1241

RAZVODOVSKAYA, L. V., GRAPOV, A. F., ARIPOV, AKIL, and MEL'NIKOV, N. N.,  
All-Union Scientific Research Institute of Chemical Agents of Plant Protec-  
tion

[Abstract] To determine whether the amino- or imino-form, or a mixture of tautomers is the form of existence of substituted ureas, heterylphosphinylureas containing monocyclic moieties of heterocycles, aromatic and nonaromatic, were studied. In synthesizing phosphorylated heterylureas, use was made of the reaction of isocyanatophosphonates and thiophosphonates with the following heterocyclic amines: 2- and 4-aminopyridine, 4-methyl-2-aminopyrimidine, 2-aminothiazole and 2-aminothioazoline. The reactions were conducted in an anhydrous solvent at temperatures from -5 to 25°. Phosphinylisocyanation of heterocyclic amines was found to occur at the exocyclic nitrogen atom. Phosphorylated and thiophosphorylated pyridyl- and pyrimidylureas exist in the amino-form in the crystalline state and in solution. Their thiazolinyl analog exist in the imino-form and in crystals and solutions. Phosphinylthiazolylurea in solution exists in the imino-form and in crystals--in the amino-form; the thiophosphinyl derivative is always in the amino-form.  
References 11: 7 Russian, 4 Western.

USSR

UDC 547.26'118

## REACTION OF DERIVATIVES OF TRIVALENT PHOSPHORUS WITH ACIDS

Leningrad ZHURNAL OBSCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1234-1238

GAZIZOV, T. KH., KHARLAMOV, V. A., PASHINKIN, A. P., and PUDOVIK, A. N.,  
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov and Kazan'  
Branch of the USSR Academy of Sciences

[Abstract] A nuclear magnetic resonance study of the reaction of  $^{31}\text{P}$ -labeled triethylphosphite with dry hydrogen chloride showed that in the absence of solvents (samples prepared at -70° and spectra were recorded at -40°) showed that the chemical shift of the phosphorus atom in the intermediate product depends on the ratio of the starting products. Formation of a P-protonated intermediate product when the reagent ratio reached 1:1 shows that protonation of triethylphosphite with hydrogen chloride occurs at a single center--the phosphorus atom. The extent and nature of protonation of the phosphorus atom of trivalent phosphorus derivatives depends on the substituents surrounding the phosphorus atom and on acid strength. Formation of a P-protonated intermediate product was observed also from the reaction of diethylchlorophosphine with hydrogen chloride. Acetaldehyde and ethanol were other

reactants used with triethylphosphite. References 13: 7 Russian, 6 Western.

USSR

UDC 547.26'118

REACTION OF ALKYL(ARYL)DICHLOROPHOSPHINES AND TETRAALKYLDIAMIDOPHOSPHONITES  
WITH ORTHO-AMINOPHENOL

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1230-1234

PUDOVIK, M. A., TERETN'YEVA, S. A., ANOSHINA, N. P., and PUDOVIK, A. N.,  
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov and Kazan'  
Branch of the USSR Academy of Sciences

[Abstract] A study was made of the reactions of phenyldichlorophosphite,  
alkyl(aryl)dichlorophosphines and diamidoalkyl(aryl)phosphonites with o-amino-  
phenol and the possible formative pathways for spirophosphoranes with a phos-  
phorus-carbon bond. The reaction products of the first two starting products  
are 5-phenyl(alkyl)-1,6-dioxa-4,9-diaza-2,3,7,8-dibenzo-5-phosphaspiro-[,4,]  
nonanes. Their formation is a consequence of the catalytic action of the  
chlorophosphines on 2-phenyl(alkyl)-4,5-benzo-1,3,2-oxazaphospholanes. Infra-  
red and nuclear magnetic resonance spectra of <sup>31</sup>P-labeled reaction products  
were recorded. References 6: 3 Russian, 3 Western.

USSR

UDC 547.241+547.391.1

MECHANISM OF THE REACTION OF ETHYLDICHLOROPHOSPHINE WITH METHACRYLIC ACID

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 47(109) No 6, Jun 77 pp  
1226-1230

GAZIZOV, T. KH., PASHINKIN, A. P., KHARLAMOV, V. A., KOVALENKO, V. I., and  
PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye.  
Arbuzov, and Kazan' Branch of the USSR Academy of Sciences

[Abstract] The mechanism of the reaction of ethyldichlorophosphine with  
methacrylic acid was studied at 35° by infrared spectroscopy. Because the  
first and second phases of the reaction follow a bimolecular mechanism, the  
reaction was studied in excess ethyldichlorophosphine (reagent ratio 31:1)  
to reveal intermediate reaction products. These products were found to be  
acid chlorides, ethylphosphonous and methacrylic acids and their addition  
compound. Hydrogen chloride was shown to strongly affect the mechanism and  
the rate of this reaction. References 4 (Russian).

USSR

UDC 542.91:541.69:547.1'118

REACTION OF O ETHYL-S-(BETA-ALKYLMERCAPTOETHYL)BENZYLTHIOPHOSPHONATES AND THEIR IODOMETHYLATES WITH CHOLINESTERASES

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHMICHESKAYA in Russian No 8, 1977 pp 1868-1872

AGABEKYAN, R. S., BERKHAMOV, M. KH., GODOVIKOV, N. N., KUZAMYSHEV, V. M., MUZYKANTOVA, V. N., BEKANOV, M. KH., and KABACHNIK, M. I., Institute of Organoelemental Compounds, USSR Academy of Sciences

[Abstract] Anticholinesterasic properties of O-ethyl-S-(beta-alkylmercaptoethyl)benzylthiophosphonates  $C_6H_5CH_2(C_2H_5O)P(O)SCH_2CH_2SR$  and their iodomethylates  $C_6H_5CH_2(C_2H_5O)P(O)SCH_2CH_2\overset{+}{S}(R)(CH_3)$ . I were investigated to find why the iodomethylates inhibit the catalytic activity of anticholinesterase only irreversibly. The rate of irreversible inhibition of cholinesterases by organophosphorus compounds was found to depend not only on the electrophilic phosphorylating ability of the inhibitor and its tendency to hydrophobic sorption on the active surface of the enzyme, but also on the complementarity of the hydrophobic substituents of the inhibitor to this surface. References 7 (Russian).

USSR

UDC 541.124:547.1'118

ACID-BASE PROPERTIES OF PHOSPHORUS COMPOUNDS. REPORT 13. REACTION OF DIPHOSPHORYL COMPOUNDS WITH NITRIC ACID

Moscow IZVESTIYA AKADEMII NAUK SSSR--SERIYA KHMICHESKAYA in Russian No 8, 1977 pp 1773-1778

NESTEROVA, N. P., ZARUBIN, A. I., MATROSOV, YE. I., MEDVED', T. YA., and KABACHNIK, M. I., Institute of Organoelemental Compounds, USSR Academy of Sciences

[Abstract] Reactions of nitric acid with dioxides of alkylidenediphosphines and their phosphonic analogs were investigated by thermometric titration and infrared spectroscopy, in continuing work on bidentate organophosphorus complexating agents. These compounds were studied: dioxides of tetraphenylvinylidenediphosphine of cis- and trans-structure, dioxide of tetraphenylmethylenediphosphine, dioxide of tetraphenylethyleneidiphosphine, tetraethyl ester of ethylenediphosphonic acid, tetraethyl ester of trans-vinylidenediphosphonic acid and vinylidiphenylphosphine oxide. Thermometric titration was conducted with nitric acid in chloroform and dichloroethane solutions. The reaction of  $HNO_3$  with the compounds listed proceeds at both phosphoryl groups, forming H-complexes of composition 2:1. Heats of formation of these complexes in  $CHCl_3$  were determined. Complexes with  $HNO_3$  were isolated in crystalline form

and their infrared spectra were studied for some of the compounds investigated. References 9: 6 Russian, 3 Western.

USSR

UDC 547.241+543.51

#### FIELD MASS SPECTRA OF PHOSPHITES

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 13 No 6, Jun 77 pp 1141-1144

LABINTSEV, V. B., GUSEV, YU. K., GRISHIN, N. N., CHISTOKLETOV, V. N., and PETROV, A. A., Leningrad Technological Institute imeni Lensoveta and Leningrad Technological Institute of the Cellulose and Paper Industry

[Abstract] The decomposition potential of five phosphite compounds was estimated by ionizing the molecules in an electric field with high potential gradient: trimethylphosphite, triethylphosphite, diethylpropylphosphite, tripropylphosphite and triisopropylphosphite. Field mass spectra of these compounds were found to have much fewer lines than electron collision spectra. Over the full range of field strengths, there were no peaks corresponding to intramolecular rearrangement processes. Observed peaks for fragmental ions corresponded to processes of simple bond rupture; bonds were broken in the first stages of breakdown of the molecular ion. Stability of alkylphosphites to a strong electric field was found to decrease with increase in alkyl substituent chain length. The P-O bond in autoionization conditions is stronger than the O-C bond. Energy acquired by the bond owing to polarization by the field is one to two orders of magnitude smaller than the rupture energy of this bond. References 9: 7 Russian, 2 Western.

USSR

UDC 547.241:547.565.2:620.197.3

INHIBITOR ACTIVITY OF THE PRODUCT OF THE REACTION OF PYROCATECHOL WITH  
DIMETHYLPHOSPHITE

Riga IZVESTIYA AKADEMII NAUK LATVIAN SSR. SERIYA KHMICHESKAYA in Russian  
No 3, 1977 pp 366-367

DREYMAN, YA. A., LUKEVITS, O. K., and MAY, L. A., Institute of Inorganic  
Chemistry, Latvian SSR Academy of Sciences

[Abstract] Corrosion inhibitor activity was studied for three compounds: pyrocatechol, dimethylphosphite and the product of the reaction of pyrocatechol with dimethylphosphite. Tests were made in these media: solutions in distilled water; salt solution simulating sea water; and solutions in 1 percent phosphoric acid. Rust-free steel plates (25x100x1 mm) were weighed and lowered into the corresponding medium. After 20 days, the plates were removed, dried, then the corrosion products were weighed after removal with a hard rubber scraper. Pyrocatechol showed weak corrosion inhibition at a concentration of 0.001 M. The reaction product was corrosion-inhibiting in the concentration range of 0.005-0.01 M. In contrast, dimethylphosphite promotes corrosion. In the salt solution, the reaction product was inactive; pyrocatechol showed very weak inhibition. In 1 percent H<sub>3</sub>PO<sub>4</sub> the reaction product is three times better in its inhibitor activity than pyrocatechol. References 1 (Russian).

USSR

UDC 547.27.118+547.444.2

REACTION OF O,O-DIETHYL-O-ACETYLPHOSPHITE WITH METHYLGlyOXAL

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 235 No 3, 1977 pp 585-588

GAZIZOV, T. KH., KIBARDIN, A. M., MUSINA, A. A., ZININ, V. N., and PUDOVIK,  
A. N., Corresponding Member of the USSR Academy of Sciences, Institute of  
Organic and Physical Chemistry of the Kazan' Branch of the USSR Academy of  
Sciences

[Abstract] The reaction of O,O-diethyl-O-acetylphosphite with methylglyoxal was investigated while studying the mechanisms of the reactions of derivatives of trivalent phosphorus with alpha-dicarbonyl compounds. The reaction with methylglyoxal was conducted in absolute ether at -20° for 10 hr; formed was a mixture of diethyl-alpha-acetoxy-beta-keto-propylphosphonate, diethyl-beta-methyl-beta-acetoxyvinyl- and diethyl-alpha-methyl-beta-acetoxyvinylphosphates. The mixture has a constant boiling point (129.5°, at a pressure of 3 mm). Total yield was 61 percent. The mixture ratio of the three products was 2.5:2. 1:1. Data showed that the reaction of O,O-diethyl-O-acetylphosphite with methylglyoxal begins with the attack of the phosphorus atom of the acylphosphite group on the carbon of the aldehyde group of methylglyoxal. References 10: 6 Russian, 4 Western.

USSR

UDC 547.953+547.455

2-GLYCO-1,3,2-DIOXAPHOSPHORINANES. SYNTHESIS AND PHENOMENON OF DIASTEREOMERIC ANISOCHRONICITY IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF  $^{31}\text{P}$

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 235 No 3, 1977 pp 595-598

INFANT'YEV, E. YE., PREDVODITELEV, D. A., GRACHEV, M. K., and SHIN, V. A.,  
Moscow State Pedagogic Institute imeni V. I. Lenin.

[Abstract] Data are presented on the synthesis of phosphorinanes using carbohydrates containing acetal and ester shielding. Phosphorylation was conducted with acid chlorides or with amides of the corresponding 1,3-alkylene-phosphorous acids. Both methods showed good glycophosphorinane yields, but the latter starting product was preparatively more convenient. Monosubstituted phosphorinanes resemble other glycoamidophosphites symmetrically substituted at the phosphorus atom in not exhibiting diastereomeric anisochronicity. Diastereomeric anisochronicity can be detected for noncyclic phosphites and amidophosphites of carbohydrates containing three different substituents at the phosphorus atom, for example, for benzyl-diethylamidophosphate of 1,2;3, 4-diisopropylidene-D-galactopyranose. References 7: 5 Russian, 2 Western.

USSR

UDC 541.67:547.241

DIPOLE MOMENT OF DIETHYL-1-(DIETHOXYPHOSPHONYL)ETHYLPHOSPHATE AND THE MOMENT OF THE GROUP  $\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$

Riga IZVESTIYA AKADEMII NAUK LATVIAN SSR. SERIYA KHMICHESKAYA in Russian  
No 3, 1977 pp 367-368

MAY, L. A., and LUKEVITS, O. K., Institute of Inorganic Chemistry, Latvian  
SSR Academy of Sciences

[Abstract] The dipole moment of diethyl-1-(diethoxyphosphonyl)ethylphosphate was found to be 3.20 D with an error of approximately  $\pm 0.05$ -0.08 D, widely differing from the dipole moment of 4.50 D found earlier for its precursor compound, the tetraethyl ester of 1-hydroxyethane-1,1-diphosphonic acid. Dipole moments were tabulated for a series of compounds incorporating the  $\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  grouping; analysis of the values showed that the dipole moment of the group  $\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  can be regarded as constant. References 5: 3 Russian, 2 Western.

## Pesticides

USSR

UDC 632.95.028 : 502.7

### METHODOLOGICAL PRINCIPLES OF PESTICIDE ECOTOXICOLOGY

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 6, 1977 pp 67-73

SOKOLOV, M. S., Candidate in Agricultural Sciences, and ECHKALOV, A. P., Institute of Agrochemistry and Soil Science, Academy of Sciences USSR

[Abstract] The two basic drawbacks of pesticide use are the development of resistant strains and the proliferation of "new" harmful organisms through disturbances of the natural balance, and contamination of the biosphere. The present study summarizes dangers of growing resistance and other aspects of selectivity related to pesticide effects, suggesting that biodegradable pesticides result in less resistance increases and other lasting effects. Natural zones that require study, as determined by the on-going "Man and the Biosphere" project, are specified, and the methodological and procedural steps to be taken are summarized. Biological monitoring of key effects and side effects of pesticides should include measurements of soils, waters, plant life and decaying matter as well as fauna that are especially sensitive to contamination. Strict methods of chemical control of non-virulent residues are also required to prevent any possibility of sepsis and poisoning of humans or domestic animals. References 26: 19 Russian, 7 Western.

USSR

UDC 632.95 : 502.7

### ORGANISMS AS INDICATORS OF ENVIRONMENTAL POLLUTION BY PESTICIDES

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 6, 1977 pp 52-55

VAS'KOVSKAYA, L. F., Institute of Zoology, Academy of Sciences Ukrainian SSR

[Abstract] A study was made of pollution caused by stable organic chloride pesticides in 1973-1976 as found in the systems of 15 rodents, 3 insectivorous mammals, 14 birds, 5 fish, 6 reptiles and 2 invertebrates, using chromatography. Soils, water samples and plants were also analyzed to establish residual amounts of pesticides. Although the pesticides sought had been banned or restricted, DDT was found in 100 percent of the analyses and hexachlorocyclohexane in 30 percent of the tests. Accumulation was found to depend on lipid content and composition, sex, time of year, species of animal, and the degree of contamination of the natural environment. It was determined that various species could serve to measure natural contamination, but only to a point where they absorbed no further amounts of pesticides, even though those levels might not cause death. Earthworms were especially good indicators of pesticides in the soil. Various mice proved to be useful indicators of contamination of agricultural and forest lands. Tables 2; references 4: 1 Russian, 3 Western.

USSR

UDC 632.95 : 502.7

PESTICIDES AND THE ENVIRONMENT: PYRETHRINES AND PYRETHROIDS

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 6, 1977 pp 39-52

KOROTKOVA, O. A., Doctor of Chemical Sciences, and PROMONENKOV, V. K., All-Union Scientific Research Institute for Chemical Means of Plant Protection

[Abstract] In seeking effective pesticides that quickly break down in the environment, esters of chrysanthemum and pyrethrinic acids were studied along with other natural pyrethrines and synthetic pyrethroids to determine the effects of light and temperature on their properties. Tests were conducted to determine the danger of preparations from these substances for mammals, including humans. The substances were found to decompose by a breakdown of the ester bonds, with hydrolysis occurring 20-30 times more rapidly in trans-isomers than in cis-isomers. Descriptions are presented of chemical reactions of these substances with methyl and benzyl alcohols and of products of oxidation and hydroxylization. Natural pyrethrines, alpha-(+)-trans-alletrine, tetrametrine and dimetrin were found to decrease in toxicity after 24 hours of exposure to light. Toxicity of pyrethrines for mammals was determined more by the lability of the ether phase than by oxidase action, and esterases which caused hydrolysis of pyrethroids were less active in preparations from insects than those from mice. Side effects on mice and other animals are summarized. The tests showed pyrethroids to have low toxicity for warm-blooded animals and to have no lingering environmental effects. Tables 8; references 33: 2 Russian, 31 Western.

USSR

UDC /661.7:547.261'185'221'13/.002.237

IMPROVEMENT OF THE TECHNOLOGY OF PRODUCTION OF METHYLDICHLOROTHIOPHOSPHATE

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 8, 1977 pp 577-579

YERMOLAYEV, V. V., and KRAVCHENKO, S. I.

[Abstract] The method of statistical planning of experiments was used to study the influence of parameters of the process on the synthesis of methyl-dichlorothiophosphate (dichloride), an intermediate in the synthesis of a number of poisons. The influence of dosing time of the components of the reaction and holding time of the reaction mass, alcohol charge, quantity of water used to wash the reaction mass, washing time and synthesis temperature on the content of the primary substance, content of  $\text{PSCl}_3$  in the product and yield of dichloride as dichloromethylthiophosphate were studied. Based on the data produced, the following mode was suggested for the production of methyldichlorothiophosphate: 172.9 g of phosphorus thiotrichloride and 125.5 g of methyl alcohol are simultaneously fed into a reactor over 20 minutes at 18-20 C with continuous agitation. Upon completion of input, the reaction mass is held for 50-55 minutes at the same temperature, then washed with

150 g water for 10 minutes. The organic layer is separated from the aqueous layer, weighed and analyzed chromatographically. The content of the primary substance in the methyldichlorothiophosphate is 93-94%, the yield of the product is 86%, about 17 and 14% higher than the corresponding indicators reached under industrial conditions. References 3 (Russian).

USSR

UDC 632.936

#### BIOLOGICAL ACTIVITY OF PHENYLGERANYL ESTERS AS JUVENILE HORMONE ANALOGUES

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 8, 1977 pp 35-37

OLESHCHENKO, I. N., STELANOVA, B. I., SVISHCHUK, A. A., and MAKHNOVSKIY, N. K.

[Abstract] A study was made of the influence of the location of the  $-OCH_3$ ,  $-CH_3$  and  $-isoC_3H_7$  radicals in the phenyl cycle of phenylgeranyl esters on the biological activity of these compounds with respect to certain insects. It was found that the activity of the aromatic terpenoid esters increased significantly when they were epoxidized. Epoxidation of the two double bonds of the phenylgeranyl ester increased the juvenile activity (in comparison to monoepoxidized ester) for some insects. The nature of these substituents and their location in the aromatic ring also had a varying influence depending on the insect used in the test. This indicates that a large number of test objects must be used in the search for juvenile hormone analogues. References 7: 1 Russian, 6 Western.

USSR

UDC 632.954:633.491

#### THE EFFECT OF HERBICIDES ON WEEDS, VIRAL DISEASES AND ON POTATO PESTS IN KUYBYSHEV OBLAST

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 8, 1977 pp 32-34

LEONT'YEVA, YU. A., KOSHELEV, S. I., and KOSHELEVA, A. B., Kuybyshev Agricultural Institute

[Abstract] Results are presented from 4-year experiments which determined the influence of mechanical processing and herbicides on the weediness of potato fields, the spread of viral diseases and the size of the population of certain potato pests. The experiments were performed in heavy loam soil, ordinary chernozem of moderate thickness and humus content. It was found that the use of eptam and the amine salt of 2, 4-D helped in successful weed control, allowed less mechanical working of the soil, the spread of viral

diseases and increased the yield. The use of promethrine and propazine also reduced the spread of viral diseases and the population of some pests somewhat, but was ineffective in combating weeds, which was reflected in a reduced harvest. References 9: 6 Russian, 3 Western.

USSR

UDC 615.282:547.785.5].012.1

SYNTHESIS AND FUNGICIDAL ACTION OF SUBSTITUTED 2-ALPHA-FURYL BENZIMIDAZOLES  
AND THEIR PHARMACOLOGICAL STUDY

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 7, 1977 pp 28-30

POZHARSKIY, F. T., (deceased), SIMONOV, A. M., OLEYNIKOVA, YA., and YEL'CHANINOV, M. M., Rostov University

[Abstract] A series of 2-(furyl-2')-benzimidazoles were synthesized and their antifungal activity was investigated. The synthesis was conducted with organolithium compounds of furan. 1-Methyl-2-(5'-lithium-furyl-2')-benzimidazole was prepared by the reaction of 1-methyl-2-(5'-bromofuryl-2')-benzimidazole with butyl lithium. Other compounds in the series were prepared by the action of benzonitrile, benzaldehyde, benzophenone and iodine on the organolithium compound of 1-methyl-2-(5'-lithiumfuryl-2')-benzimidazole. Antifungal activity of several compounds in the series was characterized by their effect on growth of *T. rubrum* culture. The compounds synthesized showed only limited antifungal activity. References 5 (Russian).

Pharmacology and Toxicology

USSR

UDC 612.419.014.24:612.6.052).014.46:691.175

STUDY OF CYTOGENETIC ACTIVITY OF POLYMERIC STRUCTURAL MATERIALS

Moscow GIGIYENA I SANITARIYA in Russian No 7, Jul 77 manuscript received 27 Dec 76 pp 38-41

BOKOV, A. N., GUS'KOVA, S. I., and GUS'KOV, YE. P., Rostov Medical Institute

[Abstract] Cytogenetic studies, under model conditions, of structural polymers, employing the anaphase method of counting chromosome aberrations in rat bone marrow cells showed that 8 of 16 tested products caused a reliable rise in chromosome damage. The other 8 induced increase in the number of fragments but otherwise did not vary from the control. The data justified the conclusion that the threshold of cytogenetic, combined action of the chemical substances, as revealed by the anaphase method is apparently lower than the general toxic action of these combined substances, and, cytogenetic studies ought to be included as one of the essential stages of a hygienic evaluation of structural polymers. The metaphase method, though more difficult to use, provided more complete information on the degree and character of the damage to genetic material of rat bone marrow cells under the influence of prolonged inhalation of complex mixtures of the chemical substances. It appears expedient to prepare test samples for both anaphase and metaphase analysis. The examination should begin with the anaphase method; if an increase in the total level of chromosome damage in cells of bone marrow tissue is established, the polymeric material should be designated as genetically active, and no further studies are needed. If the anaphase method is inconclusive, the metaphase method should be used. The three polymeric materials tested for the metaphase method were two triple laminates based on polyester resin PN-1, and relin based on synthetic rubber SKB-35 RShCh. References 5 (Russian).

USSR

UDC 615.281(Diocidum)].099.07

STUDY OF THE TOXICITY OF DIOCIDE AND ITS CONSTITUENTS

Moscow KHMIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 7, 1977 pp 44-49

PROYNOVA, V. A., NECHUSHKINA, L. V., LIS, M. B., and BESSONOVA, N. I., Branch of the All-Union Scientific Research Chemical-Pharmaceutical Institute imeni S. Ordzhonikidze, and Novokuznetsk Scientific Research Chemical-Pharmaceutical Institute

[Abstract] Diocide consists of a mixture of ethanolmercurichloride (one part) and N-cetylpyridinium chloride or bromide (two parts). Cetylpyridinium chloride is an inversion detergent with high antibacterial activity; it is a white odorless hygroscopic powder, cream-hued, readily soluble in water at room temperature and more rapidly--with heating to 50° C. Ethanolmercurichloride is a mercury antiseptic. It is a white odorless substance,

crystallizing in plate form; its melting point is 155° C and it dissolves in boiling water in a 1:60 ratio. In the toxicity study, experiments were conducted on white mice, rats, rabbits and guinea pigs (ten animals in each group). Acute and subacute toxicity was studied by daily dosing (0.5 ml each dose) of the constituents and the complete mixture by spraying the nasal mucosa with an 0.1 percent (group one) and an 0.2 percent diocide solution. Organ and cytological examinations showed that diocide and ethanolmercurichloride (EMC) are classified as highly toxic substances, and cetylpyridinium chloride (CPC)--as moderately toxic. But since the preparations are low in volatility, intoxication with saturated vapor in production conditions is not highly probable. The preparations, especially EMC and diocide, have a pronounced local-irritant and skin-resorptive action. Calculated maximum allowable concentrations are as follows: 0.1 mg/m<sup>3</sup> for CPC dust and 0.01 mg/m<sup>3</sup> for EMC in the air of the working zone. The threshold concentration for single inhalation exposure to EMC dust is 8 mg/m<sup>3</sup>. References 4 (Russian).

USSR

UDC 576.851.142.06 + 616.981.142-036.22

AEROMONADES IN FOOD PRODUCTS AND THEIR POSSIBLE ROLE IN THE RISE OF FOOD TOXINFECTI0NS

Moscow GIGIYENA I SANITARIYA in Russian No 8, Aug 77 pp 97-100

KALINA, G. P., Prof, Moscow Scientific-Research Institute of Hygiene imeni F. F. Erisman

[Abstract] Long known as disease-producing agents in cold-blooded animals, the aeromonades are now definitely known to attack higher animals, including man. At the present time the clinical manifestations of aeromonadosis, and also its epidemiological patterns of infection, are being studied. The clinical manifestations assume three basic forms: enteritis of various degrees of severity, local processes of a suppurative or necrotic character, and septicemia, which is severe and often fatal. Aeromonades usually play the role of secondary agents, and complicate some basic illness which would be present in their absence. Samples of the microorganisms taken from human patients are highly virulent for animals, in which they produce plasmocoagulase, a fibrinolytic enzyme, leukocidin and hyaluronidase. As revealed by Soviet research since the early 1970's, the primary sources of the organisms are certain foods such as sausage, milk, cream and fish, and drinking water; neither preservation nor other treatments, as ordinarily practiced, entirely remove aeromonades from these items of diet. The authors studied an outbreak of food toxinfection, and concluded that aeromonades were present as a contributory factor. Clinical details are summarized. References 15: 3 Russian, 12 Western.

USSR

UDC 615.917'222

TOXICOLOGICAL FEATURES OF CERTAIN CHLORINE DERIVATIVES OF HYDROCARBON

Moscow GIGIYENA I SANITARIYA in Russian No 8, 1977 pp 50-53

TSULAYA, V. R., BONASHEVSKAYA, T. I., ZYKOVA, V. V., SHAYPAK, V. M., ERMAN, F. M., SHORICHEVA, V. N., BELYAYEVA, N. N., KUMPAN, N. N., TARASOVA, K. I., and GUSHINA, L. M., Institute of General and Communal Hygiene imeni Sysin, Academy of Medical Sciences USSR, Moscow

[Abstract] Several chlorinated hydrocarbons--1,2-dichloropropane (DCP), per-chloroethylene (PCE) and 1,2,3-trichloropane (TCP)--are among the air-contaminants now being discharged by the chemical industry during production of organochlorine compounds, synthetic glycerine and vinylchloride. In addition, some chlorinated hydrocarbons are now being widely used as solvents in the chemical industry, in the synthesis of organic compounds, and in agriculture as insecticides. Despite the possibility of extensive and dangerous contamination by these substances, very little is so far known about their toxicity, and no data at all have been published on the effect of small concentrations. The authors ran tests to determine the toxic action of the three above compounds, using white male rats as test animals subjected to long-term inhalation at two concentrations: PCE, 4.2 and 20.0 mg/m<sup>3</sup>; DCP, 1.5 and 10.0 mg/m<sup>3</sup>; and TCP, 0.4 and 2.0 mg/m<sup>3</sup>. None of the compounds showed any effect on the weight dynamics of the animals. Mean values of erythrocyte content remained normal. Hemoglobin content was not appreciably affected. However, at the three higher concentrations, functional changes were observed in the central nervous system and in the central nervous system and in the activity of blood enzymes, as well as structural shifts in the liver, lung and mast-cell systems, and disruption of the bioenergy processes in the liver, lungs and suprarenals. There were also changes in the DNA-synthesizing system of the liver. The smaller concentrations did not produce any statistically reliable indications of similar changes. References 7: 4 Russian, 3 Western.

Polymers and Polymerization

USSR

UDC 677.4.014.2:543

THE TOXICITY AND COMPOSITION OF COMBUSTION PRODUCTS OF CERTAIN CHEMICAL AND NATURAL FABRICS AND FIBERS

Moscow KHMICHESKIYE VOLOKNA in Russian No 4, 1977 pp 49-51 manuscript received 16 Jul 77

EYTINGON, A. I., PODDUBNAYA, L. T., NAUMOVA, L. S., and GRIBUNOVA, G. P.

[Abstract] Toxic properties of airborne combustion products were measured at three temperatures, 300, 600 and 850° C, with minimal period of effect at 5 minutes, using white mice. The test fabrics were burned in a 0.5 l/min air stream. Toxic effects were measured in terms of saturation by by-products relative to mortality of 50%. Acetochlorine fabrics and polyvinylchloride fabrics produced hydrogen chloride, while fibers of the phenol type produced phenol and aldehydes. These caused death 2-3 days after exposure. Other fibers tested, including wool, had immediate effects, and survivors of 3-5 minutes were still alive after 14 days. Results indicated that the highest toxicity of combustion by-products came with woolen fabrics, aromatic polyamides, polycaprolactam fiber, and viscous fibers with flame retardants. The most lethal by-products were carbon monoxide, hydrogen cyanide and hydrogen chloride. References 7: 2 Russian, 5 Western.

USSR

UDC 678.5.029.46:677.463-96.004.14

THE USE OF MODIFIED CHEMICAL FIBERS TO GIVE FLAME RESISTANCE TO PHENOL PLASTICS

Moscow KHMICHESKIYE VOLOKNA in Russian No 3, 1977 pp 42-43 manuscript received 10 May 76

ARTEMENKO, S. YE., BILKOVA, S. A., and TYUGANOVA, M. A.

[Abstract] One promising method of giving plastic materials flame resistance is that of reinforcing standard synthetic resins with modified chemical fibers, particularly flame resistant viscose fibers. Viscose fibers can be made non-flammable by introducing various phosphorus or halogen-containing compounds. This article describes the results of investigation of a plastic based on an aniline-phenolformaldehyde resin and various flame resistant viscose fibers. The fibers were rated by determining the percentage of fiber which must be included in the fiber-plastic composite material to provide good overall flame resistance. In the particular case tested, 45-50% by mass of the modified viscose fiber was sufficient to make the composites fireproof. References 5: 4 Russian, 1 Western.

East Europe

EAST GERMANY/WEST GERMANY

CONTRIBUTIONS TO THE CHEMISTRY OF PHOSPHORUS. PART 65. DATA ON THE CYCLO-CARBA-PHOSPHANES  $(PC_6H_5)_4CH_2$ ,  $(PC_6H_5)_4CH_2S$ , AND  $(PC_6H_5)_4CH_2S_2$

Leipzig ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 431 No 1, Jun 77 pp 39-48 manuscript received 10 Aug 76

BAUDLER, M., professor, Dr, VESPER, J., Dr, KLOTH, B., graduate chemist, KOCH, D., and SANDMANN, H., Institute of Inorganic Chemistry, University, Koeln

[Abstract] This article describes and interprets the  $^{31}P$  and  $^1H$  nuclear magnetic resonance spectra of  $(PPh)_4CH_2$  and the reaction of this compound with sulfur resulting in the formation of the thio-cyclo-carba-phosphanes  $(PPh)_4CH_2S$  and  $(PPh)_4CH_2S_2$ . The two latter compounds are the first true derivatives of a hetero-cyclo-phosphane, specifically of the cyclo-monocarba-phosphane. In contrast to pentaphenyl-cyclopentaphosphane, cyclo-monocarba-phosphane reacts with sulfur in a 4:1 ratio and does not involve ring change or P-S-P bridge formation. Instead, the ring system of the starting compounds remains intact and a true exocyclic addition of the sulfur on a phosphorus atom near the  $CH_2$  group takes place. Even in reaction at a 2:1 ratio, the sulfur only adds to the intact ring system of the starting compound. All the foregoing indicate that the heterocyclic  $P_4C$  skeleton is more stable than the homocyclic  $P_5$  skeleton. Figures 2; table 1; references 18: 6 Western, 12 German.

EAST GERMANY/WEST GERMANY

CONTRIBUTIONS TO THE CHEMISTRY OF PHOSPHORUS. PART 66. CRYSTAL AND MOLECULAR STRUCTURE OF 1,2,3,4-TETRAPHENYL-CYCLO-5-CARBA-1,2,3,4-TETRAHOSPHANE,  $(PC_6H_5)_4CH_2$ , AND 1,4-DITHIO-1,2,3,4-TETRAPHENYL-CYCLO-5-CARBA-1,2,3,4-TETRAHOSPHANE,  $(PC_6H_5)_4CH_2S_2$

Leipzig ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 431 No 1, Jun 77 pp 49-60 manuscript received 10 Aug 76

BAUDLER, M., and LEX, J., Institute of Inorganic Chemistry, Koeln University

[Abstract] The compounds in the title were examined for their crystal and molecular structure by X-ray analyses.  $(PC_6H_5)_4CH_2$  forms monoclinic crystals (Space Group Cc;  $a = 22.272$ ,  $b = 13.726$ ,  $c = 7.492 \text{ \AA}$ ;  $\beta = 96.82^\circ$ ; number of units in the basic cell: 4).  $(PC_6H_5)_4CH_2S_2$  forms triclinic crystals (Space Group  $\bar{P}1$ ;  $a = 10.900$ ,  $b = 10.663$ ,  $c = 12.233 \text{ \AA}$ ;  $\alpha = 100.04^\circ$ ,  $\gamma = 70.65^\circ$ ; number of units in the basic cell: 2). Molecular-structural diagrams and tabulated

data about atomic coordinates (with standard deviations), coefficients of the temperature factors of the phosphorus, carbon, and hydrogen atoms, bond lengths, and bond angles (with standard deviations) are presented. Tables 13; figures 41; references 9: 5 Western, 4 German.

EAST GERMANY/WEST GERMANY

#### SILYLPHOSPHINOBORANES

Leipzig ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 32 No 1, Jun 77 pp 61-75 manuscript received 5 Jul 76

FRITZ, G., professor, Doctor, and HOELDERICH, W., Doctor, Institute for Inorganic Chemistry, Karlsruhe University

[Abstract] This article describes the reactions of metallized disilyl phosphanes with boron halides which lead to the first defined silyl-phosphinoboranes, and the cleavage reactions of the  $(\text{me}_3\text{Si})_3\text{P}$  with boron halides, which in certain cases also leads to the formation of silylphosphinoboranes. Specifically, it describes the reaction between  $(\text{me}_{3-n}\text{SiH}_n)_2\text{PLi} \cdot \text{OR}_2$  and  $(\text{me}_2\text{N})_2\text{BCl}$ , the reaction between  $(\text{me}_3\text{Si})_2\text{PLi} \cdot \text{OR}_2$  and  $(\text{me}_2\text{N})\text{BCl}_2$ , the reaction between  $(\text{me}_3\text{Si})_2\text{PLi} \cdot \text{OR}_2$  and  $(\text{C}_6\text{H}_5)_2\text{BBr}$  or  $(\text{C}_6\text{H}_5)\text{BCl}_2$ , and the reaction between  $(\text{me}_3\text{Si})_3\text{P}$  and  $(\text{C}_6\text{H}_5)_2\text{BBr}$ . The silylphosphineboranes obtained were examined by means of nuclear magnetic resonance spectrometry ( $^1\text{H-NMR}$ ). Data on the synthesis and NMR spectra are presented. The tests are supplemented with mass spectrometric examinations. Figures 2; tables 4; references 11: 3 Western, 8 German.

EAST GERMANY/WEST GERMANY

FORMATION OF DISILYLPHOSPHINO-ELEMENT COMPOUNDS OF C, Si, AND P

Leipzig ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE in German Vol 431 No 1, Jun 77 pp 76-87 manuscript received 5 Jul 76

FRITZ, G., Professor, Doctor, and HOELDERICH, W., Doctor Institute of Inorganic Chemistry, Karlsruhe University

[Abstract] The reactions of  $(\text{me}_3\text{Si})_2\text{PLi} \cdot \text{OR}_2$  with some halides of C, Si, and P are described. The non-halide reactants are used in the form of their THF adducts. The reactions between  $(\text{me}_3\text{Si})_2\text{PLi} \cdot 2\text{THF}$  and carbon halides, the reactions between metallized disilylphosphanes and silicon halides, and the reactions between metallized disilylphosphanes and phosphorus halides are described. The cleavage of tris-(trimethylsilyl)phosphane with phosphorus halides is discussed. The products were examined with the aid of  $^1\text{H}$  nuclear magnetic resonance spectrometry. Experimental synthesis data are given in detail. The significance of these syntheses is that the starting compound is readily accessible. Figures 3; tables 3; references 16: 6 Western, 1 Russian, 9 German.

HUNGARY

UDC 632.95.028:543."71"

DEVELOPMENT TRENDS IN PESTICIDE RESIDUE ANALYSIS

Budapest MAGYAR KEMIKUSOK LAPJA in Hungarian Vol 32 No 4, 1977 pp 186-189

PFEIFER, GYULA, Research Institute for the Heavy Chemical Industry, Veszprem

[Abstract] The work of the pesticide laboratories established in the various districts of Hungary is regulated by the Main Department of Plant Protection of the Ministry of Agriculture and Food. These laboratories study the decomposition rate of the pesticides when present as residues, establish waiting times for foods, regularly monitor domestically sold foods for pesticide residue content, and examine imported foods for pesticide residues. Most analytical methods are either spectrophotometric or chromatographic (primarily gas-chromatographic). They vary in their sensitivities and specificities. There is extensive literature dealing with the methods and their performance and application. Future research trends include better structural analysis of the pesticides, development of methods requiring less sample preparation, and standardization. In Hungary it is thought that the future belongs to gas chromatography/mass spectrometry techniques, which permit large numbers of samples to be analyzed quickly and accurately. Instrument design and construction is an important activity that the Hungarian instrument industry is engaged in. Tables 3; references 8: 1 German, 1 Hungarian, 6 Western.

HUNGARY

UDC 632.95.001.5/.6 "313"

NEW TRENDS IN PESTICIDE RESEARCH

Budapest MAGYAR KEMIKUSOK LAPJA in Hungarian Vol 32 No 4, 1977 pp 190-193

TUSKE, MARTON, Research Institute for Plant Protection, Budapest

[Abstract] This article is the text of the author's lecture delivered at the 16th Regional Conference of the Biochemistry Section of the MKE [Association of Hungarian Chemists], Debrecen, 1976. Based on references in the literature, a survey is presented about the latest research trends in the field of pesticides. The following subjects are discussed: the needs of agriculture for pesticides, the biological mechanisms of the pesticides, research for improved pesticides, growth regulators, antidotes against growth regulators, third-generation pesticides and insecticides, chitin-synthesis inhibitors, nutrition and oviposition inhibitors, pheromones and antipheromones, hormone analogs and antihormones, juvenile hormone analogs, juvenile hormone antagonists, shedding hormone analogs, shedding hormone antagonists, and chemosterilizing agents. The goal of all these studies is to develop pesticides with optimum performance characteristics. References 39: 4 Hungarian, 4 German, 31 Western.

CSO: 1841

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